Reprinted from Journal of the Air & Waste Management Association, Vol. 42, No. 9, September 1992

Ozone Control Strategies Based on the Ratio of Volatile Organic Compounds to Nitrogen Oxides

Wolff Korsog 1992

George T. Wolff and Patricia E. Korsog
General Motors Research and Environmental Staff
Warren, Michigan

The 1990 Clean Air Act Amendments require states with O_3 nonattainment areas to adopt regulations to enforce reasonable available control technologies (RACT) for NO_x stationary sources by November 1992. However, if the states can demonstrate that such measures will have an adverse effect on air quality, NO_x requirements may be waived. To assist the states in making this decision, the U.S. EPA is attempting to develop guidelines for the states to use in deciding whether NO_x reductions will have a positive or negative impact on O_3 air quality. Although NO_x is a precursor of O_3, at low VOC/NO_x ratios, the reduction of NO_x can result in increased peak O_3. EPA is examining existing information on VOC/NO_x ratios to develop "rules of thumb" to guide the states in their decision-making process. An examination of 6 a.m. to 9 a.m. VOC/NO_x ratios at a number of sites in the eastern U.S. indicates that the ratio is highly variable from day-to-day and there is no apparent relationship between ratios measured at different sites within the same area. In addition, statistical analysis failed to identify significant relationships between the 6 a.m. to 9 a.m. VOC/NO_x ratio and the maximum 1-hr. O_3 within a given area. Since we know from smog chamber and modeling studies that such a relationship exists, this further invalidates the assumption that a ratio measured at a single site is representative of the ratio for the entire region. Based on this information, we conclude that having the 6 a.m. to 9 a.m. ambient VOC/NO_x ratio for a given area is insufficient information, by itself, to decide whether a VOC-alone, a NO_x-alone, or a combined VOC-NO_x reduction strategy is a viable or optimum O_3-reduction strategy.

Implications

The 1990 Clean Air Act Amendments require that ozone nonattainment areas adopt regulations to reduce stationary-source NO_x emissions unless it can be demonstrated that the implementation of such regulations would have a deleterious effect on air quality. Whether NO_x emission reductions will have a benefit or disbenefit on O_3 air quality depends largely on the local VOC/NO_x ratio, and it was the hope that decisions to adopt (or not to adopt) NO_x rules could be based on existing VOC/NO_x ambient air data. However, the analysis presented here indicates that existing VOC/NO_x ambient data are not adequate to use as a basis for making this decision. It is recommended that a state-of-the-art photochemical grid model be used to determine the appropriate strategy.

Three decades of research have clearly demonstrated that volatile organic compounds (VOCs), nitrogen oxides (NO_x) and sunlight are needed to produce the high concentrations of ozone (O_3) observed in many areas of the U.S. during the warmer part of the year.[1] This research has also shown that the O_3 formation process is extremely nonlinear, and that under certain conditions (low VOC/NO_x ratios), additional NO will destroy O_3 rather than contribute to its formation.[1–6] In addition, at low ratios, NO_x (NO and NO_2) scavenges free radicals that otherwise would have reacted with VOCs to eventually produce O_3. This behavior of NO_x in reducing O_3 is known as the "NO_x inhibition effect."

In formulating the 1990 Clean Air Act Amendments, Congress recognized the "NO_x inhibition effect." For all O_3 nonattainment areas, the Amendments require the states to submit to the U.S. Environmental Protection Agency (EPA) their NO_x "reasonable available control technology" (RACT) and "new source review" (NSR) rules by November 1992, unless the "net air quality benefits are greater in the absence of reductions of oxides of nitrogen from the sources concerned."[7] The Amendments also direct EPA to issue guidelines to the states by November 1991 to help them determine whether NO_x reductions will have a net air quality benefit or disbenefit. (As of this writing, the EPA guidelines have not been developed). Given the November 1992 deadline for rule submission, the states will have to decide whether or not to adopt the NO_x rules sometime in early 1992 unless some means to allow them additional time to investigate this issue is found. As a result, they may have to make the decision without having the time to employ the best available scientific tool, a photochemical grid model. The serious, severe, and extreme nonattainment areas are required to run the grid models, but the results are not required until their November 1994 State Implementation Plan (SIP) submittals.[8]

Previously, EPA recommended that areas with a 6 a.m. to 9 a.m. VOC/NO_x ratio of 10:1 (10 ppb carbon per 1 ppb NO_x) or greater consider NO_x reductions, while areas with a lower ratio employ VOC reductions alone.[3] (It should be noted that existing strategies have actually been a combined VOC-NO_x reduction strategy, not a VOC-alone strategy because of the NO_x emission reductions mandated by the federal and California state motor vehicle emission programs. From 1980 to 1989, NO_x emissions from highway vehicles nationwide decreased 25 percent, but total NO_x emissions declined just 5 percent as stationary source emissions have increased.) The basis for this recommendation can be seen by examining a typical O_3 isopleth diagram shown in Figure 1. The first region in the upper left is the NO_x-inhibition region. In this region, a decrease in NO_x alone results in an increase in O_3, but a decrease in VOC (labeled hydrocarbons in Figure 1) decreases O_3. The region

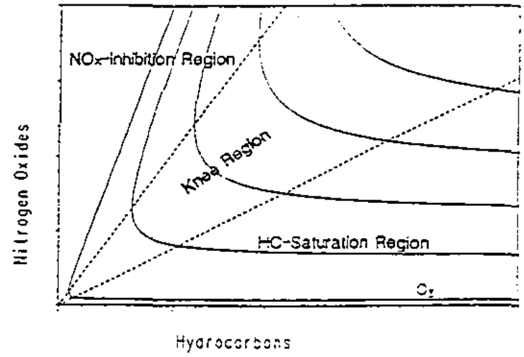

Figure 1. Typical O_3 isopleth diagram showing the three chemical regimes. The 6 a.m. to 9 a.m. NO_x concentrations are plotted on the y-axis and the 6 a.m. to 9 a.m. VOC (labeled hydrocarbon) concentration is plotted on the x-axis. Ozone concentrations increase with increasing distance from the origin in the knee region.

at the bottom right is the VOC saturation region where reducing VOCs has no effect on the O_3. On the other hand, a reduction in NO_x in this region results in lower O_3. In the middle is the knee region, where reductions in either reduce O_3. A ratio of 10:1 is usually near the center of the knee. The upper and lower boundaries of the knee region will vary from day-to-day and from place-to-place as its location is a function of the reactivity of the VOC mix and the sunlight intensity. Large urban areas in northern parts of the U.S. typically have ratios less than 10 while smaller cities and suburban areas, as well as cities in the southern U.S., typically have higher ratios.[3] However, in order to use a measured 6 a.m. to 9 a.m. ratio to make control strategy decisions, it must be assumed that: (1) the mean or median measured ratio adequately characterizes the ratio for the highest O_3 days, (2) the afternoon O_3 maximum is dependent upon the morning ratio in the source area, and (3) the spatial variability of the ratio within the source area is small.

The purpose of this report is to examine existing 6 a.m. to 9 a.m. VOC/NO_x ratio data to see if these assumptions are valid. Specifically, the following questions are addressed: (1) What is the distribution of ratios at a given site? (2) Are the ratios much different on high O_3 days as compared to low O_3 days? (3) Are there any statistical relationships between the afternoon maximum O_3 and the 6 a.m. to 9 a.m. ratio in the source area? and, (4) How does the ratio vary spatially within a given urban area?

Methodology

EPA Data Base

Measurements of VOCs are not routinely made as part of any of the permanent air monitoring networks because of the labor-intensive nature of the sampling and analysis methodologies. However, in 1984, EPA began a VOC-sampling program in a number of cities around the U.S.[9] Each summer EPA chooses approximately a dozen cities and collects the 6 a.m. to 9 a.m. ambient air on weekdays for several weeks. The samples are analyzed for individual volatile organic compounds which are summed to obtain the total VOC concentration.[10] Since the program is still continuing, many cities have data for more than one summer. At most of the sites concurrent NO_x data are also available, and the ratios at these sites have been summarized by Baugues.[11–13] If concurrent VOC and NO_x data were not available from the same site, the site was not used in this analysis. We accessed these data as well as the O_3 data from the AIRS data base[14] and from Baugues.[15]

Table I. Sampling sites.

Site	Years	Comments
Philadelphia	84, 86	urban
Cleveland	85, 88	urban
St. Louis	85, 87–88	urban
Baltimore	86	urban
Atlanta1	84, 87	urban
Atlanta2	87	urban (Decatur, GA)
NNJ1	88	urban (Newark, NJ)
NNJ2	88	suburban (Plainfield, NJ)
NYC1	88	urban (Manhattan)
NYC2	88	urban (roof of the World Trade Center)

The 6 a.m. to 9 a.m. VOC/NO_x data were paired with the 1-hour maximum afternoon O_3 concentration at the same site if it was available. If it was not available, an O_3 site which was typically downwind was chosen. The choice of the O_3 site was not considered to be critical for this analysis because within a given urban area, intersite afternoon O_3 maxima are highly correlated.[16,17]

Selection of Sites

A number of cities in the eastern half of the U.S. were included in this analysis. The sites chosen are shown in Table I along with the years in which data were available.

Data Editing

Since background O_3 is normally between 30 and 50 ppb, any day with a 1-hour O_3 maximum of less than 30 ppb is suspect, and hence was eliminated. Likewise, VOC and NO_x concentrations less than 100 ppb and 5 ppb respectively were eliminated because they are too close to the noise level of the analytical methodology, and for NO_x, positive interferences are likely to be significant at these levels. After these editing changes were made to the data base, the VOC/NO_x distributions were visually examined; unexplained high-end outliers were found to exist in the St. Louis data set. For St. Louis, there were 173 observations with a ratio less than 21 and five with a ratio between 30 and 56. None of these high ratio days had O_3 above 80 ppb. Since contamination cannot be ruled out, and since these outliers would have a significant impact on certain statistics (i.e., means and correlations), they were eliminated.

Results

Summary Statistics

The means, standard deviations, medians and ranges of the ratios are summarized in Table II. It is apparent from the large values of the standard deviations that there is considerable variability in the ratio. This becomes even more obvious when the frequency distribution diagrams of

Table II. Summary statistics.

	VOC/NO_x					
Site	N	Mean	Std. Dev.	Median	Max.	Min.
Philadelphia	79	7.7	8.9	5.4	57.5	1.7
Cleveland	132	7.4	2.5	7.0	17.5	2.2
St. Louis	178	9.9	3.3	9.7	20.6	1.3
Baltimore	66	5.8	3.4	6.1	16.0	0.7
Atlanta1	110	10.2	5.0	9.2	27.0	2.8
Atlanta2	76	9.4	4.7	7.9	28.7	3.9
NNJ1	77	7.7	2.3	7.3	16.2	3.0
NNJ2	78	10.8	3.1	10.0	20.3	5.7
NYC1	67	9.2	4.1	8.6	24.3	3.5
NYC2	25	14.8	12.8	11.4	53.2	2.2

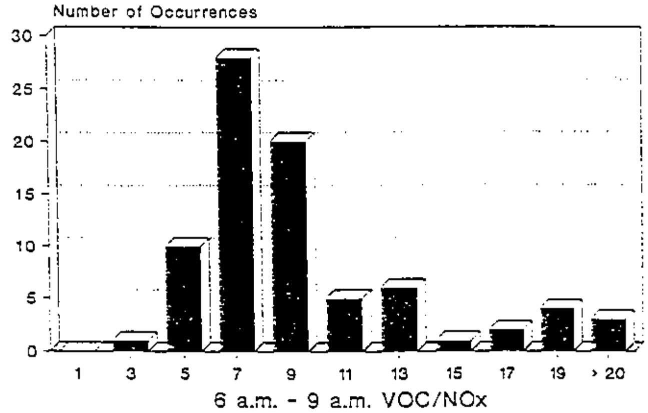

Figure 2. VOC/NO_x distribution at Atlanta2.

the ratios are viewed. The shape of the frequency distributions are similar from site-to-site. A typical one is shown for Atlanta2 in Figure 2. For distributions that are this skewed, the median value is a better measure than the mean for the "most-likely-value" of the ratio. Consequently, our discussions will focus on the medians.

The medians at all sites except NNJ2 (Plainfield, NJ) and NYC2 (the roof of the World Trade Center) are less than 10. Following EPA's previous guidelines, this would indicate that VOC reduction strategies alone would be the recommended policy for all sites except these two.[3] This applies even to Atlanta where a strong case has recently been made for a NO_x reduction strategy.[19] However, given the wide dispersion of the ratio, the representativeness of the median ratio, especially on high O_3 days, is of concern.

It is not surprising that the median ratios are greater than 10 in Plainfield and on top of the World Trade Center. Plainfield is a suburban area located about 30 km upwind (to the southwest) of heavily urbanized Newark. Suburban areas tend to have higher ratios than urban areas because suburban areas usually have a higher fraction of biogenic VOCs, and they tend to experience a more "aged" air mass. An "aged" air mass will have a higher ratio than fresh emissions because the NO_x reacts more quickly than the bulk of the VOCs. Consequently, the NO_x is depleted more rapidly than the VOCs. Because the monitors on top of the World Trade Center are located approximately 305 m above street level, the air that is sampled is usually partially-aged emissions from upwind New Jersey, rather than fresh ground-level emissions from Manhattan.

Table III. Effect of ozone on the ratio.

Site	All obs.	Median VOC/NO_x High O_3#	Median VOC/NO_x Low O_3
Philadelphia	5.4	7.1*	5.0
Cleveland	7.0	9.0**	6.8
St. Louis	9.7	10.4**	9.4
Baltimore	6.1	6.5	5.8
Atlanta1	9.2	9.7	9.1
Atlanta2	7.9	7.9	8.1
NNJ1	7.3	8.0	6.9
NNJ2	10.0	11.9**	9.6
NYC1	8.6	10.5**	7.9
NYC2	11.4	18.3	9.7

High O_3 days are defined as those days with the 1-hour daily maximum in the upper quartile of observations. The 75th percentiles are: Philadelphia—90 ppb; Cleveland—73 ppb; St. Louis—73 ppb; Baltimore—92 ppb; Atlanta1—128 ppb; Atlanta2—128 ppb; NNJ1—99 ppb; NNJ2—87 ppb; NYC1—70 ppb; NYC2—110 ppb.
** High O_3 median ratio is significantly higher than low O_3 median at $p \le 0.10$.
* Same as ** except at $p \le 0.20$.

Table IV. Correlation coefficients between the 6 a.m. to 9 a.m. VOC/NO_x ratio and the 1-hr. maximum O_3.

Site	Correlation
Philadelphia	0.12
Cleveland	0.16**
St. Louis	0.03
Baltimore	0.03
Atlanta1	0.07
Atlanta2	−0.08
NNJ1	0.17
NNJ2	0.20*
NYC1	0.06
NYC2	0.09

** Significant at $p \le 0.05$.
* Significant at $p \le 0.10$.

High O_3 Versus Low O_3 Days

The ratios, stratified into high and low O_3 days, are summarized in Table III. A high O_3 day for a given site is defined as a day with the 1-hour maximum O_3 concentration in the upper quartile of observations for that site. The 75th percentiles for each site are given in the first footnote to Table III. All other days are classified as low O_3 days. The medians can be compared using the two-sample Wilcoxon Rank Sum test,[18] which is a nonparametric procedure that tests whether or not there is a difference between the central location parameters (the median in this case) of two independent samples. The median ratios on high O_3 days are higher at nine of the ten sites, and the differences are statistically significant (depending on the significance level chosen) at only 4 or 5 of the sites. Also, the correlations between the ratio and the 1-hr. maximum O_3 concentrations (summarized in Table IV) are, at best, weak. The highest correlation is only 0.20 at the NNJ2 site, and only the correlations at NNJ2 and Cleveland are significant at p (significance level) ≤ 0.10. At all other sites the correlation coefficients were lower, and none even came close to being significant at this level. Visual examination of scatterplots of O_3 versus the ratio failed to provide any clues as to why there was no relationship. Consequently, although the median ratios tend to be slightly higher for the high O_3 days at most sites, the statistical relationships are not strong enough to develop reliable quantitative relationships.

At some of the sites, a somewhat stronger relationship appears to exist between the 1-hr. maximum O_3 and the 6 a.m. to 9 a.m. concentrations of precursors. The data in Table V show that the median values for VOCs are higher at all sites on the high O_3 days, and the difference is significant at seven of the sites. NO_x is also higher at most of the sites as well, and this difference is significant at six of the sites. In addition, significant correlations exist between the pre-

Table V. 6 a.m. to 9 a.m. median VOC and NO_x concentrations.

Site	VOC (ppb) High O_3	VOC (ppb) Low O_3	NO_x (ppb) High O_3	NO_x (ppb) Low O_3
Philadelphia	674**	314	83**	62
Cleveland	1031**	770	121**	116
St. Louis	712**	519	73**	55
Baltimore	653**	532	92	92
Atlanta1	729	600	65	64
Atlanta2	505	380	56	49
NNJ1	917**	579	131**	79
NNJ2	640**	394	60**	42
NYC1	919**	607	94**	70
NYC2	469	178	20	16

** High ozone median concentration is significantly higher than low O_3 median at $p \le 0.10$.

Table VI. Correlation coefficients between the 1-hr maximum O_3 and the 6 a.m. to 9 a.m. VOC and NO_x concentrations.

Site	Correlation Coefficients		
	VOC-O_3	NO_x-O_3	VOC-NO_x
Philadelphia	0.14	0.27**	0.47**
Cleveland	0.48**	0.34**	0.79**
St. Louis	0.27**	0.26**	0.46**
Baltimore	0.11	−0.001	−0.10
Atlanta1	0.24**	0.12	0.78**
Atlanta2	0.25**	0.20**	0.79**
NNJ1	0.52**	0.42**	0.91**
NNJ2	0.26**	0.26**	0.89**
NYC1	0.34**	0.34**	0.73**
NYC2	0.36**	0.15	0.65**

** Significant at $p \leq 0.05$.
* Significant at $p \leq 0.10$.

cursors themselves, as well as with O_3, at all of the sites except Baltimore (Table VI). This apparent relationship between high afternoon O_3 and high concentrations of 6 a.m. to 9 a.m. precursors does not prove cause and effect, however. Previous studies[17,20,21] in the eastern U.S. have shown that high afternoon O_3 concentrations are usually associated with poor morning mixing conditions (low wind speeds). Such conditions would also be conducive for the accumulation of morning emissions including VOCs and NO_x. This is further supported by the data in Table VI which show much stronger correlations between the morning NO_x and VOCs than with either precursor and the afternoon O_3.

Spatial Relationships

The relationships among the pollutants and the ratio at the three paired sites are quite different. In Atlanta, one site is in downtown (Atlanta1) while the other is about 7 km east of downtown Atlanta in urban Decatur (Atlanta2). Since there is a continuous urban corridor between Atlanta and Decatur, similar VOC/NO_x ratios would not be unexpected. The data in Table II indicate that, on the average, the ratio at Atlanta1 is less than one unit higher than at Atlanta2, and this difference is not significant at $p \leq 0.10$. Comparisons of the medians under a variety of conditions given in Table III show that the medians in Atlanta are always within two units of each other. A somewhat different picture is presented in Table VII, however. Although significant intersite correlations exist for VOC, NO_x, and especially for O_3, the weak intersite correlation for the ratio is not significant.

For the NNJ sites, the NNJ2 (Plainfield) site is 30 km upwind (on the prevailing SW wind) of NNJ1 (Newark), and between the two sites there is about 20 km of suburban landscape. Consequently, a somewhat higher ratio would be expected in NNJ2, and this is what is observed in Tables II and III. The median ratio at NNJ2 is significantly higher at $p \leq 0.05$. Despite the 30 km distance between the sites, the intersite correlations for VOC, NO_x, and in particular for O_3, are excellent, but the correlation for the ratios is poor (Table VII).

The median ratio is significantly higher at NYC2 at $p \leq 0.10$. Although both NYC sites are located in Manhattan, one would expect them to be dominated by very different air masses. NYC1 is on the east side of Manhattan on a roof of a school 23 m above ground level and is dominated by ground level emissions from within Manhattan. NYC2, which is on the roof of the 100-story World Trade Center a few blocks east of the Hudson River, is probably not affected by emissions in Manhattan under the prevailing westerly wind conditions. Consequently, the air sampled at NYC2 is probably dominated by partially-aged emissions from New Jersey which would be expected to have a higher VOC/NO_x ratio than fresh emissions. This hypothesis is consistent with the means and the medians presented in Tables II and III, and the poor correlations between NO_x, VOC, and the ratio (Table VII). Only the intersite correlation for O_3 is significant, underscoring the regional nature of this species.

Table VII. Intersite correlation coefficients.

Sites	VOC	NO_x	VOC/NO_x	O_3
Atlanta1—Atlanta2	0.51*	0.70*	0.23	0.94*
NNJ1—NNJ2	0.68*	0.71*	0.07	0.85*
NYC1—NYC2	0.44	0.13	0.43	0.84*

* Significant at $p \leq 0.01$.

Discussion

The overall median ratio was less than 10 at all of the urban sites except the World Trade Center site. (Because the World Trade Center is the exception to many of the generalizations made in this discussion—for reasons presented in previous sections—no further references to this site will be made.) Previous EPA guidance would have made all of the areas candidates for VOC-only control strategies. When the median ratios for the upper-quartile O_3 days are considered instead, the median ratio at two of the sites, St. Louis and NYC1, exceeds 10. Previous EPA guidance would have made these areas candidates for a combined VOC-NO_x reduction strategy. However, recent New York State and EPA modeling results using the Urban Airshed Model (UAM)[5] and the Regional Oxidant Model (ROM)[22] respectively, strongly suggest that New York City is a clear-cut case where NO_x reductions would be counterproductive. In addition, Atlanta—a city where the evidence appears to support that NO_x reductions will reduce O_3 because of a large contribution from biogenic VOCs—has a ratio less than 10. Based upon this conflicting evidence, we conclude that decisions regarding the benefits of NO_x reductions in a given area cannot be made based on VOC/NO_x ratio data alone. Moreover, one cannot tell from the ratio the relative importance of biogenic versus anthropogenic VOC emissions. For example, if the ratio falls in the knee region (see Figure 1), but the VOCs are dominated by biogenic emissions, a VOC reduction strategy may not be sufficient by itself to achieve the required O_3 reductions.

At 9 of the 10 sites, the median ratio increased slightly in the upper quartile of O_3 days and was less than or equal to 2 ratio units higher than the overall median. Since high O_3 days are associated with high temperatures, this difference could be a result of higher evaporative emissions. Nevertheless, this relatively small difference indicates that the use of either the median or the upper quartile ratio will not significantly change the resulting control strategy if an EKMA analysis is employed. However, this small difference is somewhat misleading because it implies a relatively constant ratio for a given area. In contrast, the relatively large standard deviation and range for the ratio at any given site implies that there is a large day-to-day variation in the ratio. This is further supported by the lack of any relationship between the ratios at different sites within the same area. Given this spatial and temporal variability, we conclude that the overall median ratio from a single site should not be used to make control-strategy decisions.

In addition, statistical analysis failed to identify significant relationships between the 6 a.m. to 9 a.m. VOC/NO_x ratio and the maximum 1-hr. O_3 within a given area. Since we know from smog chamber and modeling studies that such a relationship exists, this further invalidates the assumption that a ratio measured at a single site is representative of the ratio for the entire region.

In summary, these results indicate that having the 6 a.m. to 9 a.m. ambient VOC/NO_x ratio for a given area is insufficient information, by itself, to decide whether a VOC-alone, a NO_x-alone, or a combined VOC-NO_x reduction strategy is a viable or optimum strategy. Furthermore, what may be the optimum strategy for a downwind area, may not be the optimum strategy for the urban area. The recent NRC report[23] emphasizes that O_3 concentrations can increase in the near field (in the population centers) in response to NO_x controls, but decrease in the far field. Consequently, we strongly recommend that a state-of-the-art photochemical grid model be employed to determine the optimum control strategy for a given area. Decisions regarding the adoption of NO_x reduction strategies should be postponed until the states apply a photochemical grid model for the purposes of developing their State Implementation Plan (SIP). The states could compare NO_x-reduction model runs to VOC-reduction model runs to determine the optimum control strategy. This will delay the implementation of NO_x reduction strategies in those areas that prove to need it by two years, but it will also prevent other areas from adopting counterproductive NO_x controls, and ensures that the control strategies are based on state-of-the-art science. This recommendation is consistent with the findings presented in the NRC report.

Acknowledgments

We are grateful to Keith Baugues of EPA for providing some of the VOC and NO_x data, and to Jon Heuss and Dave Aldorfer of GM's Research and Environmental Staff for their helpful comments.

References

1. Seinfeld, J. H. "Ozone air quality models—a critical review," *J. Air Waste Manage. Assoc.* **38:** 616 (1988).
2. Kelly, N. A.; Gunst, R. F. "Response of ozone to changes in hydrocarbon and nitrogen oxide concentrations in outdoor smog chambers filled with Los Angeles air," *Atmos. Environ.* **24A:** 2991 (1990).
3. Congress of the United States, Office of Technology Assessment, "Catching Our Breath: Next Steps for Reducing Urban Ozone," OTA-O-412, 1989.
4. Heuss, J. M.; Wolff, G. T. "Measurement needs for designing and assessing ozone control strategies," *Water Air Soil Pollut.* (in press).
5. Rao, S. T.; Sistla, G. "The efficacy of nitrogen oxides emissions control in ozone attainment strategies as predicted by the urban airshed model," *Water Air Soil Pollut.* (in press).
6. Milford, J. B.; Russell, A. G.; McRae, G. J. "A new approach to photochemical pollution control: implications of spatial patterns in pollutant responses to reductions in nitrogen oxides and reactive organic gas emissions," *Envir. Sci. Technol.* **23:** 1290 (1989).
7. 1990 Clean Air Act Amendments, Section 182(f).
8. U.S. EPA, "General Preamble Implementation of Title I Clean Air Act Amendments of 1990," 1992.
9. Seila, R. L.; Lonneman, W.; Meeks, S. A. "Determination of C_2 to C_{12} Ambient Air Hydrocarbons in 39 U.S. Cities from 1984 through 1986," EPA/600/3-89/058, Research Triangle Park, NC, March 1989.
10. Radian Corporation, "1990 Nonmethane Organic Compound and Three-Hour Toxics Monitoring Program," EPA No. 68D80014, Research Triangle Park, NC, January 1991.
11. Baugues, K. "A Review of NMOC, NO_x and NMOC/NO_x Ratios Measured in 1984 and 1985," EPA-450/4-86-015, Research Triangle Park, NC, September 1986.
12. Baugues, K. "Results of recent non-methane hydrocarbon measurements," paper no. 86-79.7, presented at the 1986 Annual Meeting of the Air Pollution Control Association, Minneapolis, MN, June 22–27, 1986.
13. Baugues, K. "Reconciling differences between ambient and emission inventory derived NMOC/NO_x ratios: implications for emission inventories," paper no. 91-67.5, presented at the 1991 Annual Meeting of the Air & Waste Management Association, Vancouver, BC, June 16–21, 1991.
14. U.S. EPA, "AIRS User's Guide, Volume V: Air Quality Data Retrieval," Research Triangle Park, NC, March 30, 1988.
15. Baugues, Keith, U.S. EPA (personal communication—April 1991).
16. Bruntz, S. M.; Cleveland, W. S.; Graedel, T. E.; Kleiner, B.; Warner, J. L. "Ozone concentrations in New Jersey and New York: statistical association with related variables," *Science* **186:** 257 (1974).
17. Kelly, N. A.; Ferman, M. A.; Wolff, G. T. "The chemical and meteorological conditions associated with high and low ozone concentrations in southeastern Michigan and nearby areas of Ontario," *JAPCA* **36:** 150 (1986).
18. Hollander, M.; Wolfe, D. A. *Nonparametric Statistical Methods*, John Wiley & Sons, New York, 1973, pp. 68–69.
19. Chamedies, W. L.; Lindsay, R. W.; Richardson, J. L.; Kiang, C. S. "The role of biogenic hydrocarbons in urban photochemical smog: Atlanta as a case study," *Science* **241:** 1473 (1988).
20. Wolff, G. T.; Lioy, P. J. "An empirical model for forecasting maximum daily ozone levels in the northeastern U.S.," *JAPCA* **28:** 1034 (1978).
21. Korsog, P. E.; Wolff, G. T. "An examination of urban ozone trends in the northeastern U.S. (1973–1983) using a robust statistical method," *Atmos. Environ.* **25B:** 47 (1991).
22. U.S. EPA, "Regional Ozone Modeling for Northeast Transport (ROMNET)," EPA-450/4-91-002a, Research Triangle Park, 1991.
23. National Research Council, *Rethinking the Ozone Problem in Urban and Regional Pollution*, National Academy Press, Washington, DC, 1991.

Dr. Wolff is a principal scientist, Plant Environment, General Motors Research and Environmental Staff, PO Box 9055, Warren, MI 48090. P. E. Korsog is with Automotive Emission Control, General Motors Research and Environmental Staff, PO Box 9015, Warren, MI 48090.

This manuscript was submitted for peer review on April 1, 1992. The revised manuscript was received on June 5, 1992.